

IV.C Catalysts

IV.C.1 New Electrocatalysts for Fuel Cells

Philip N. Ross (Primary Contact), Nenad Markovic, Voja Stamenkovic
Materials Sciences Division
Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720
Phone: (510) 486-6226; Fax: (510) 486-5530; E-mail: pnross@lbl.gov

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

Objectives

- Conduct research on the kinetics and mechanism of electrode reactions in low-temperature fuel cells.
- Develop new electrocatalysts using a materials-by-design approach.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

- Study the kinetics of fuel cell electrode reactions on well-characterized model electrodes and high surface area fuel cell electrocatalysts using modern electroanalytical methods.
- Study the mechanisms of the reactions using state-of-the-art in-situ spectroscopies.
- Use ultra-high vacuum (UHV) methods of surface preparation and surface analyses to form tailored surfaces.
- Synthesize nanoclusters to have the tailored surface.
- Characterize the microstructure of the nanoclusters by high-resolution electron microscopy.
- Transfer new technology to developers and/or component suppliers.

Accomplishments

- Discovered a type of bimetallic Pt catalyst that could reduce the Pt loading from current levels, i.e. near 1 g/kW, to 0.25 g/kW.

Future Directions

- Pursue the development of the new type of bimetallic Pt catalyst that has the potential to reduce Pt loading to 0.25 g/kW.
- Conduct research on the chemistry and mechanism behind the loss of Pt surface area in polymer electrolyte membrane (PEM) fuel cell cathodes during vehicle operation.

Introduction

The last decade has witnessed a tremendous growth in our understanding of chemical and electronic properties of thin metal films supported on foreign metal substrates. Modern molecular (atomic) surface characterization techniques operating under ultra-high vacuum (UHV) conditions have revealed that variations in interfacial bonding and energetic constraints produced between monolayer metal films and their substrates provide a means for modifying the chemical properties of surfaces [1]. While many different metals have been studied as monolayer films in UHV, only thin metal films of Pd have received significant attention in electrochemical studies. Another way to create monoatomic thin metal film on the host metal is to use thermodynamic driving force, which would lead to preferential surface enrichment (segregation) in one element over a core of the other, i.e. the outermost layer is a “skin” of one element. In principle, one could use this thermodynamic property to replace the “buried” atoms in Pt nanoparticles with a non-precious metal, resulting in 100% Pt dispersion (all Pt atoms are surface atoms) without the need to create extremely small particles, e.g. <2 nm. For example, if a standard pure Pt catalyst consists of particles having, on average, a dispersion of 20%, replacement of the buried atoms in those particles with a base metal would enable the Pt loading to be reduced by a factor of 5, all other factors being the same. Development and optimization of either thin metal films or nanoparticles having a “skin” microstructure is the basic strategy we are currently pursuing to reduce precious metal loading in PEM fuel cell (air) cathodes.

Approach

New electrocatalysts are being developed using a materials-by-design approach. Selection of new catalytic materials is based on research conducted on the kinetics and mechanisms of the electrode reactions using model systems, e.g. metallic single crystals, bimetallic bulk alloys and bimetallic thin films. All model system samples are prepared and characterized in a UHV chamber and transferred to electrochemical cells. Surface composition and structure is determined using a combination of surface analytical techniques, e.g. Low Energy

Electron Diffraction (LEED), Low Energy Ion Scattering (LEIS), and Auger Electron Spectroscopy (AES). Multi-metallic catalysts are synthesized under carefully controlled conditions producing tailor-made surfaces. Once a promising new catalytic material is identified in these model studies, prototype fuel cell electrodes are synthesized and tested against established benchmarks.

Results

Enhanced Specific Activity of Pt₃Co Alloy Catalysts

A correlation was found between the electronic properties of the “Pt-skin” surface structure on the vacuum-annealed Pt₃Co alloy and the specific activity (per unit Pt area) for the oxygen reduction reaction (ORR). As shown in Figure 1, the annealed surface of the Pt₃Co alloy has the highest stable activity for the ORR (under PEM conditions) of any catalyst, about 3 times that for polycrystalline Pt. The annealed Pt₃Co surface has a pure Pt outermost layer with a second layer enriched in Co (relative to the bulk), produced essentially by an exchange of Co atoms in the surface for Pt atoms in the second layer (there is also a similar exchange between the second and third layers raising the second layer concentration of Co to about 75%). The Pt atoms on this Co-enriched second layer experience a lateral in-plane compression that as shown by the experimental photoelectron energy distribution curves (EDC), shifts the valence electron (d-band) density of states (DOS). This effect of compressive stress on the valence band DOS was predicted from density functional theory (DFT) by Ruban et al. [2]. Hammer and Norskov [1] have shown that the interactions between adsorbates and transition metal surfaces involve the entire d-band. They suggested that a convenient metric which captures the interaction with the entire d-band is the “d-band center”, the first moment of the DOS from the Fermi level. This metric from our EDCs, as noted in Figure 1, shows a clearly significant shift of the d-band center for the annealed Pt₃Co surface, the most active catalyst. The shift in d-band center we observed experimentally is in remarkably good agreement with that calculated from DFT by Norskov and co-workers [3] for the same Pt-Co surface. A further correlation from the Norskov theory is that this shift in d-band center weakens the interaction of the

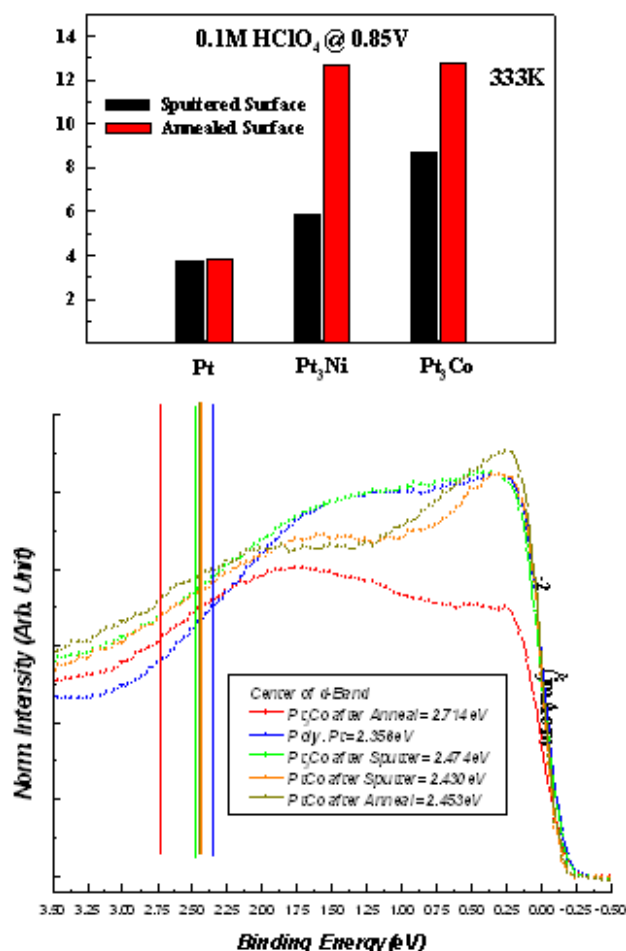


Figure 1. Correlation of the activity of bulk Pt₃Co alloy (above) for oxygen reduction to the valence band density of states using the d-band center as metric (as suggested by Norskov and co-workers [2]).

surface Pt atoms with adsorbates like O and H [1]. We propose here that the weaker interaction with OH_{ad} reduces the steady-state coverage by this species, which is a site-blocking species in the ORR and increases the reaction rate. We have confirmed in emersion experiments (removing the sample from electrolyte and examining the surface in UHV) that the Pt-skin structure of the annealed surface of Pt₃Co is stable to potentiodynamic cycling from 0 - 1.0 V at PEM conditions. Monte-Carlo simulations also indicate that the Pt-skin structure is the thermodynamically preferred microstructure in Pt₃Co nanoparticles, i.e. as in the practical fuel cell catalyst.

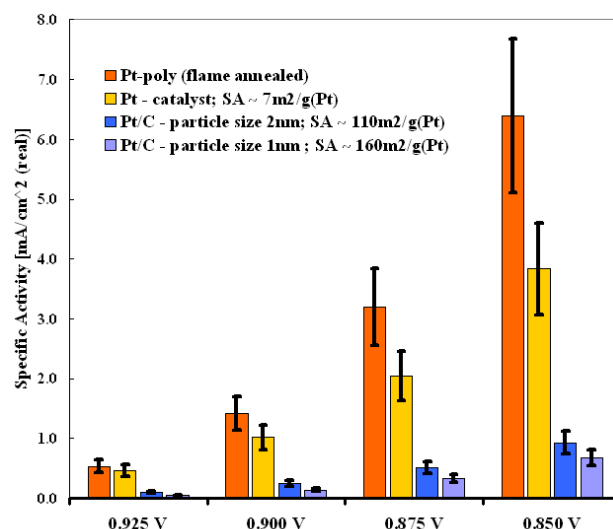


Figure 2. The effect of Pt particle size on the specific activity (per unit Ptarea) for oxygen reduction at different potentials.

The Crystallite Size Effect in the ORR

Improvements in the precision of measuring reaction rates and Pt surface areas enabled us to re-examine the question of the relation between Pt crystallite size and the kinetics of the ORR. This effect was studied relatively extensively for hot phosphoric acid [4], but not for PEM or simulated PEM conditions. Some recent results from our laboratory are shown in Figure 2. The effect is in fact quite similar to that reported for phosphoric acid [4,5], with nanoparticles of Pt having specific activities (per unit Pt surface atom) about one-fifth that of bulk polycrystalline Pt. Kinoshita [4] suggested that the dependence of activity on particle correlated with the fraction of the nanoparticle surface that has (100) facets, i.e. assuming that (111) facets and edge and corner atoms are significantly less active than atoms in (100) facets. At that time, there were no data for the ORR on Pt single crystal surfaces in hot phosphoric acid to corroborate this correlation. We therefore have re-investigated the structure-sensitivity of the ORR on Pt single crystals in simulated PEM fuel cell conditions. The results are shown in Figure 3. It is clear that the structure-sensitivity is, in fact, not that strong, and the sensitivity is actually opposite to that inferred by Kinoshita, i.e. [110] > [111] > [100]. Extensive analysis of the microstructure of Pt particles by

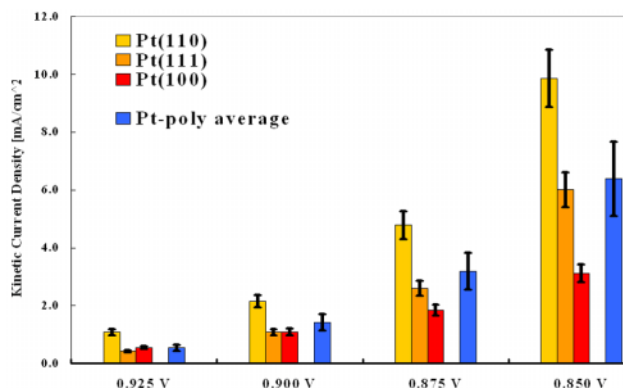


Figure 3. Structure sensitivity of the oxygen reduction reaction on Pt surfaces in 0.1 M HClO₄ at 60°C.

transmission electron microscopy, an example of which is shown in Figure 4, does support Kinoshita's assumption of cubo-octahedral shape, but the variation in the surface geometry with particle size, also shown in Figure 4, together with the differences in activity for different surface geometries, does not explain the 5-fold increase in specific activity between Pt nanoparticles and bulk Pt. There must, therefore, be another as yet unknown reason for the particle size effect. Practically speaking, the results in Figure 3 have several beneficial consequences. These results rationalize the performance in fuel cells of the 3M unsupported Pt "whisker" catalysts [6], which have a relatively low surface area, e.g. 7 - 10 m²/g, but come within a factor of 2 in mass activity (per g of Pt) to Pt nanoparticle catalysts having ten times higher surface area. It also rationalizes the observation that there is a large loss of Pt surface area early in the life of PEM fuel cell cathodes without a correspondingly large loss in cell performance. Indeed, there seems to be little practical benefit to increasing Pt surface area above about 60 m²/g. This surface area target could lead to simplified chemistry for catalyst preparation (and lower cost). On the other hand, loss of surface area below about 50 m²/g during operation will result in a proportionate decrease in performance, so it is imperative to minimize loss of surface area in this size regime. At present, we do not know what the crystallite size effect is for nanoparticle alloy catalysts, such as Pt₃Co. Experiments with Pt₃Co alloy nanoparticles are underway.

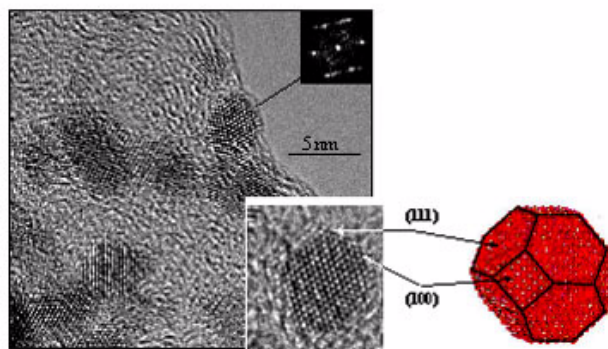
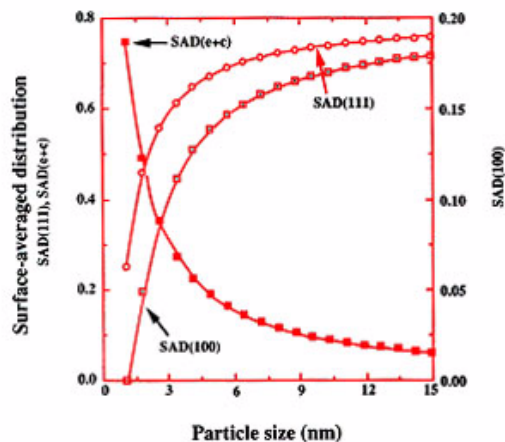


Figure 4. Distribution of low index facets and low coordination sites (edges and corners) as a function of particle size for the cubo-octahedral particles in standard carbon supported Pt electrocatalyst.

Conclusions

- A correlation was found between the electronic properties of the "Pt-skin" surface structure on the vacuum-annealed Pt₃Co alloy and the specific activity (per unit Pt area) for the oxygen reduction reaction (ORR). Kinetic models using this correlation can account for the enhanced activity of the Pt₃Co catalyst.
- The crystallite size effect for the ORR in PEM electrolyte is quite similar to that reported previously for hot phosphoric acid, with nanoparticles of Pt having specific activities (per unit Pt surface atom) about one-fifth that of bulk polycrystalline Pt.

- However, the variation in the surface geometry with particle size together with the differences in activity for different surface geometries does not explain the 5-fold increase in specific activity between Pt nanoparticles and bulk Pt. There must, therefore, be another as yet unknown reason for the particle size effect.
- These results rationalize the performance in fuel cells of the 3M unsupported Pt “whisker” catalysts, which have the relatively low surface area of 7 - 10 m²/g, but come within a factor of 2 in mass activity (per g of Pt) to Pt nanoparticle catalysts having ten times higher surface area.
- There seems to be little practical benefit to increasing Pt surface area above about 60 m²/g, which could lead to simplified chemistry for catalyst preparation (and lower cost).

References

1. B. Hammer and J. Norskov, *Adv. Catal.* **45**, 71 (2000)
2. A. V. Ruban, B. Hammer, P. Stoltze, H. Skriver, and J. Norskov, *J. Mol. Cat.* **115**, 421 (1997)
3. J. Kitchen, J. Norskov, M. Barteau, and J. Chen, *J. Chem. Phys.* **120**, 10240 (2004)
4. K. Kinoshita, *J. Electrochem. Soc.* **137**, 845 (1990) and references therein
5. M. Sattler and P. Ross, *Ultramicroscopy* **20**, 21 (1986)
6. M. Debe et al., U.S. Patent No. 5,879,827.
2. Arenz M. Stamenkovic V. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. “The electro-oxidation of formic acid on Pt-Pd single crystal bimetallic surfaces.” *Physical Chemistry Chemical Physics* **5**, 4242-4251, 2003 Oct 1.
3. Stamenkovic V. Schmidt TJ. Ross PN. Markovic NM. “Surface segregation effects in electrocatalysis: kinetics of oxygen reduction reaction on polycrystalline Pt₃Ni alloy surfaces.” *Journal of Electroanalytical Chemistry* **554**, 191-199, 2003 Sep 15.
4. Arenz M. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. “The oxygen reduction reaction on thin palladium films supported on a Pt(111) electrode.” *Journal of Physical Chemistry B* **107**, 9813-9819, 2003 Sep 11.
5. Arenz M. Stamenkovic V. Ross PN. Markovic NM. “Preferential oxidation of carbon monoxide adsorbed on Pd submonolayer films deposited on Pt(100).” *Electrochemistry Communications* **5**, 809-813, 2003 Sep.
6. Arenz M. Stamenkovic V. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. “The effect of specific chloride adsorption on the electrochemical behavior of ultrathin Pd films deposited on Pt(111) in acid solution.” *Surface Science* **523**, 199-209, 2003 Jan 10.
7. Schmidt TJ. Stamenkovic V. Ross PN. Markovic NM. “Temperature dependent surface electrochemistry on Pt single crystals in alkaline electrolyte - Part 3. The oxygen reduction reaction.” *Physical Chemistry Chemical Physics* **5**, 400-406, 2003.

FY 2004 Publications/Presentations

Refereed Journals

1. Schmidt TJ. Stamenkovic V. Markovic NM. Ross PN. “Electrooxidation of H₂, CO and H₂/CO on well-characterized Au(111)-Pd surface alloys.” *Electrochimica Acta* **48**, 3823-3828, 2003 Nov 15.
8. Stamenkovic V. Schmidt TJ. Ross PN. Markovic NM. “Surface composition effects in electrocatalysis: Kinetics of oxygen reduction on well-defined Pt₃Ni and Pt₃Co alloy surfaces.” *Journal of Physical Chemistry B* **106**, 11970-11979, 2002 Nov 21.

Books and Book Chapters

1. Markovic NM. Radmilovic V. Ross PN. "Physical and Electrochemical Characterization of Bimetallic Nanoparticle Electrocatalysts", in *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, Ed. Wieckowski A. Savinova ER. Vayenas CG, Marcel Dekker, New York and Basel, 2003, Chapter 9, pp. 311-342.
2. Ross, PN. "Oxygen Reduction Reaction on Single Crystal Electrodes", in *Handbook of Fuel Cells: Fundamentals, Technology and Applications, Volume 2, Electrocatalysis*, Ed. Viestich W. Lamm A. Gasteiger H., John Wiley & Sons Ltd., Chichester, 2003, pp. 465-481.

Special Recognitions & Awards/Patents Issued

1. 2003 Hydrogen, Fuel Cells and Infrastructure Technologies R & D Award to Dr. Philip Ross in recognition of outstanding achievement in research and development of electrocatalysts for PEM fuel cells.